

PATENT SPECIFICATION

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(54) PROCESS FOR PRODUCING TEREPHTHALIC ACID

(71) We, MITSUI PETROCHEMICAL INDUSTRIES LTD., a Japanese body corporate of 2-5, 3-chome, Kasumigaseki, Chiyoda-ku, Tokyo, Japan, do hereby declare
 5 the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
 10 This invention relates to a process for the production of terephthalic acid which is of sufficiently high quality to be used in the production of fibre grade polyesters by the direct polymerisation method.
 15 There is a known process for producing terephthalic acid which comprises oxidising para-xylene at elevated temperatures and pressures in the liquid phase with molecular oxygen or a gas containing molecular oxygen
 20 in the presence of acetic acid and a cobalt-containing catalyst, condensing the gaseous oxidation reaction product, which contains a non-condensable gas, steam and acetic acid vapour, removing the non-condensable gas while recycling the condensate consisting predominantly of water and acetic acid to the oxidation reaction, crystallising the terephthalic acid in the liquid reaction product, recovering terephthalic acid crystals, distilling the mother liquor to recover acetic acid, and recycling the acetic acid to the oxidation reaction.
 25 The terephthalic acid produced by this process is not entirely satisfactory and is susceptible to discolouration. Accordingly the polyester prepared by the direct polymerisation method using this terephthalic acid was discoloured.
 30 We have now found that terephthalic acid of improved quality may be prepared by a process which comprises oxidising para-xylene in the liquid phase with either molecular oxygen or a gas containing molecular oxygen in the presence of acetic acid and a cobalt-containing catalyst, recovering terephthalic acid by crystallisation from the liquid oxidation reaction product, recycling to the oxidation reaction without distillation the mother

liquor, which contains catalyst, remaining after removal of crystalline terephthalic acid, passing the gaseous oxidation reaction product which contains non-condensable gas, water vapour and acetic acid vapour through a fractionating zone in which the acetic acid vapour is condensed while the water vapour is not condensed, recycling the condensed acetic acid to the oxidation reaction and removing the water vapour, together with the non-condensable gas, from the reaction system. In the process of the present invention, therefore, a condensate containing both water and acetic acid is not recycled to the oxidation reaction as in the case of the prior art process and, further, the mother liquor remaining after removal of crystalline terephthalic acid is not distilled to recover acetic acid. Although it is not quite clear why terephthalic acid of improved quality results from the process of the invention, it is thought the impurities which are the primary cause of discolouration of the product, are removed by the fractional distillation of the gaseous reaction product containing non-condensable gas, steam and acetic acid. In the prior art method the condensate containing impurities, water and acetic acid is recycled to the reaction system. Also in the prior art process the accumulation in the oxidation reaction system of the water that forms during the reaction is thought to participate in the formation of impurities.

In addition to making possible the production of terephthalic acid of improved quality, the process of the invention simplifies control of the water content of the reaction system, increases the rate of the oxidative reaction and reduces the rate of decomposition of the acetic acid. Another advantage is that the mother liquor remaining after separation and recovery of terephthalic acid crystals need not be distilled to recover the acetic acid for recycling to the reaction.

The cobalt-containing catalysts to be used in the oxidation reaction are known. The cobalt catalysts may be used alone or they

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can be used in conjunction with other heavy metal oxidation catalysts, e.g. compounds of such heavy metals as manganese, chromium and nickel. The cobalt-containing catalysts 5 may also be used in conjunction with a bromine-containing catalyst and such known reaction accelerators as acetaldehyde and methyl ethyl ketone. A preferred catalyst contains cobalt, manganese and bromine.

The cobalt-containing catalyst can be metallic cobalt or an inorganic or organic compound of cobalt, but preferably is used in a form in which it is soluble in the reaction system. Suitable cobalt compounds are cobalt acetate, cobalt naphthenate and cobalt bromide. Manganese compounds which may also be used include manganese acetate and manganese naphthenate, while bromine compounds which can be used are sodium bromide and calcium bromide.

There is no particular restriction on the amount of the cobalt-containing compound and suitable amounts are of the order of 0.01—50% by weight based on the weight of the starting para-xylene.

As well as molecular oxygen there can be used a gas containing molecular oxygen such as mixtures of oxygen and an inert gas such as nitrogen and carbon dioxide. Commercially, air is usually used. The amount of gas employed preferably is such that the amount of molecular oxygen is in excess of the stoichiometric amount. The amount to be used can be determined from the concentration of molecular oxygen in the non-condensable gas leaving the reaction system which preferably is of the order of at least 2% by weight, especially 3—20% by weight.

The liquid phase oxidation of the invention 40 is generally carried out, as in the prior art method, at elevated temperatures and pressures. Suitable temperatures are 100—300° C., preferably 150—170° C., and suitable pressures are super-atmospheric pressures up to 150 kg/cm² gauge.

The amount of acetic acid used, as reaction solvent, is not critical but preferably is from 2—12 parts by weight per part by weight of para-xylene starting material.

Fractional distillation of the gaseous oxidation reaction product can be carried out by providing a distillation column at a point above an exhaust vapour outlet in the upper part of the oxidation reactor. The apparatus used in the conventional method can therefore readily be adapted for use in the process of the invention by providing a distillation column instead of a condenser.

The fractional distillation operation can 60 readily be carried out by controlling the temperature of the exhaust vapour leaving the reaction zone. The temperature is controlled so that the non-condensable gas and steam pass through the fractional distillation zone.

It is usually convenient to employ an apparatus in which an oxidation reactor is coupled to a distillation column with a pipe or an apparatus in which the two units are directly joined. The distillation column may be a packed column containing a filler or, preferably, a column provided with a plurality of trays. When the oxidation reactor and the distillation column are joined together, the distillation column preferably does not have a part in which liquid is retained such as an overflow dam, in order to avoid clogging by powdered carboxylic acid which may be entrained in the exhaust vapour.

The operating conditions of the distillation column should suitably be varied in accordance with the conditions of the oxidation reaction. In general the column is operated in such a way that the amount of water in the oxidation reaction system is from 0.5 to 15% and preferably 0.5 to 10% by weight. The pressure at the top of the distillation column can be varied from normal atmospheric pressure to 50 kg/cm² gauge and the temperature from 100° to 250° C., depending upon the temperature and pressure of the oxidation reaction.

The terephthalic acid contained in the liquid oxidation product may be crystallised and recovered in any suitable manner and the known multistage crystallisation technique can be used. A particularly preferred method is one in which the liquid oxidation reaction product is flashed to cause the terephthalic acid to crystallise, coarse particles of terephthalic acid are isolated and recovered, the mother liquor containing finely divided terephthalic acid crystals is recycled to the oxidation reaction, and the coarse particles of terephthalic acid are washed with acetic acid recovered from the flashed vapour.

Flashing had to be avoided in the prior art method since any terephthalic acid remaining in the mother liquor, which was not recycled unchanged to the oxidation reaction, would have been lost, causing a reduction in the yield of terephthalic acid. Hence, the practice was to enlarge the particles of the separated terephthalic acid by carrying out the crystallisation in several stages. However, there is no reduction in the yield in the present invention even though terephthalic acid crystals may be contained in the mother liquor, since the mother liquor is recycled to the oxidation reaction zone as obtained following separation of the coarse terephthalic acid crystals. Also since finely crystalline terephthalic acid tends to contain a larger proportion of impurities than does the larger particle size material, the production of terephthalic acid of improved quality can be advantageously carried out by the flashing method. It is, of course, also possible to carry out substantially complete separation of the terephthalic acid and to recycle to the oxidation reaction a mother liquor which con-

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5	tains substantially no terephthalic acid crystals.	
10	When the oxidation reaction product is flashed the liquid product containing the crystalline terephthalic acid can be passed to a separation zone while the flashed vapour stream is withdrawn from the flashing zone, the acetic acid contained therein is condensed, and the acetic acid obtained can either be recycled directly to the reaction zone or may be used to wash the terephthalic acid crystals before being recycled.	crystallises out. While the drawing shows only one crystallisation tank, two or more may be used coupled together. Alternatively, a flashing chamber can be provided in place of the crystallization tank. The slurry containing terephthalic acid crystals is conducted from tank III via line 7 to a separator IV, where crystalline terephthalic acid is isolated from the mother liquor. The resulting terephthalic acid is withdrawn via line 8 and, if necessary, washed in acetic acid and dried to obtain the final product. The mother liquor is withdrawn from the separator IV via line 9 and is recycled to the reactor I.
15	The separated terephthalic acid crystals can be dried as they are to obtain a final product, but it is preferred to wash the crystals in acetic acid and then to dry the washed crystals to obtain the final product. The acetic acid used for washing preferably is the acetic acid obtained by flashing the reaction product and condensing the acetic acid in the flashed vapour.	The invention will be further described by reference to the following Examples.
20	The acetic acid used in the washing operation is collected and is then usually recycled to the oxidation reaction.	
25	By-products which derive from either the impurities formed during the course of the oxidation reaction or from impurities contained in the starting para-xylene gradually accumulate in the reaction system upon repeated cycling of the mother liquor. For this reason a part of the mother liquor preferably is withdrawn from the system and discarded. If necessary withdrawn mother liquor can be recycled and reused after the addition of a fresh batch of acetic acid.	Example I
30	When the reaction product is flashed a distillation zone can be provided in the crystallisation zone by means of which moisture can be distilled off.	An oxidation reactor coupled at its upper end to a distillation column provided with 30 trays is fed, at an hourly rate, with 150 kg of paraxylene, 1200 kg of 95% acetic acid and, as oxidation catalyst, 1.5 kg of cobalt acetate, 0.8 kg of manganese acetate and 1.8 kg of sodium bromide. An oxidation reaction is then carried out at 190° C. and 12 kg/cm ² gauge while introducing air into the bottom of the reactor. A vapour mixture consisting predominantly of acetic acid and steam, which evaporates during the oxidation reaction, is distilled in the column at a column top temperature of about 160° C., and the steam is removed from the top of the column along with non-condensable gas, while the condensed acetic acid is recycled. The water content of the reaction system is thus stabilized at from 3 to 4%. The oxidation reaction is carried out under these reaction conditions with an average residence time of 60 minutes.
35	The accompanying drawing is a flowsheet which illustrates the process of the invention.	The liquid oxidation product is withdrawn into a crystallisation tank and, after cooling, is separated into terephthalic acid and a mother liquor. The terephthalic acid obtained is then washed with acetic acid and dried. The mother liquor was recycled to the oxidation reactor and reused. The yield of terephthalic acid was 97 mol % based on the para-xylene, it had a colour value (Hazen number) of 18, its optical density at 38 m μ was 0.020, and its 4-carboxybenzaldehyde content was 0.12%. The colour value was obtained by dissolving 3 grams of the terephthalic acid in 20 ml of 2N sodium hydroxide and comparing the colour of this solution with the colour of a standard solution in accordance with ASTM procedure D 1209 (1969). The 4-carboxybenzaldehyde content was determined by polarography.
40	In the drawing, para-xylene, acetic acid and a cobalt-containing catalyst are fed via line 1 to an oxidation reaction apparatus consisting of an oxidation reactor I to the upper part of which is connected a distillation column II. An oxidation reaction is then carried out by introducing a gas containing molecular oxygen via line 2 at the bottom of the reactor I. A gaseous mixture, which consists predominantly of acetic acid, water and non-condensable gas leaves the top of reactor I and is conducted via line 3 to the distillation column II, where it is submitted to a fractional distillation operation. Steam and non-condensable gas are removed from the system at the top of the distillation column II while acetic acid is refluxed in the distillation column II and is recycled via line 5 to the reactor I. The liquid oxidation reaction product is withdrawn from the bottom of the reactor I via line 6 and is cooled in a crystallisation tank III, whereupon the terephthalic acid, which is soluble in acetic acid,	100
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Control I

Example I was repeated except that the distillation column at the top of the oxidation reactor was replaced by a condenser which condensed not only the acetic acid in the vapour leaving the reactor but also the steam.

5 The yield of terephthalic acid was 94 mol %, its purity was 97%, it had a Hazen number of 300; its optical density at 380 μ was 0.670, and its 4-carboxybenzaldehyde content was 1.5%.

Example II

10 An oxidation reaction was carried out as in Example I with hourly feed rates of para-xylene, glacial acetic acid and cobalt acetate of 80, 150 and 40 kg, respectively, and a reaction temperature 130° C. The water formed during the reaction was removed as steam from the top of the distillation column along with non-condensable gas, while the acetic acid was condensed and recycled. The reaction was carried out with an average residence time of 2 hours. The yield of terephthalic acid was 90 mol %, based on the para-xylene, its purity was 99%, and it had 20 a Hazen number of 80.

Example III

25 An oxidation reactor was fed with 100 kg/hr of para-xylene, 90 kg/hr of 99% acetic acid (1% water) and, as oxidation catalyst, 3.4 kg/hr of cobalt acetate, 3.4 kg/hr of manganese acetate and 1.7 kg/hr of sodium bromide, as well as 850 kg/hr of a mother liquor containing finely divided terephthalic acid of particle size less than 40 microns. An oxidation reaction was carried out with an average residence time of 60 minutes at 190° C. and at 12 atmospheres pressure while introducing air into the bottom of the reactor at the rate of 10 cubic meters per minute. A fractional distillation operation was carried out 30 on the gaseous reaction product in a distillation column of 15 trays coupled to the reactor. The fractional distillation was carried out at a column top temperature of 160° C. and a column bottom temperature of 178° C., so that steam was removed along with waste gas while the acetic acid was condensed and was recycled to the reaction zone. The water content in the oxidation reaction system was thereby maintained at about 5%. The reaction product was withdrawn from the reactor via a pressure regulating valve and was introduced to a flashing chamber at normal atmospheric pressure where it was flashed and the terephthalic acid crystallised out. The volatiles were removed from the top of the flashing chamber, while the acetic acid suspension of terephthalic acid, cooled to 120° C. by the latent heat of evaporation of the solvent in the flashing chamber was forwarded 45 to a filter of the centrifugal type. Crystalline terephthalic acid was separated by filtration from a mother liquor containing finely divided terephthalic acid of particle size less than about 40 microns (the weight ratio of the separated crystalline terephthalic acid to the finely divided terephthalic acid contained in the mother liquor was 97:3). The mother 50 55 60

liquor was recycled to the reaction zone after mixing with fresh acetic acid, para-xylene and a sufficient amount of the oxidation catalyst to replenish that lost to the system. Terephthalic acid crystals of coarse particle size containing substantially no terephthalic acid of particle size less than 40 microns was fed to a dryer after washing with acetic acid. The acetic acid used for washing was that obtained by condensing the vapour from the crystallisation step. The yield of terephthalic acid based on para-xylene was 96 mol % when the continuous oxidation reaction attained its steady operational state. The purity of the terephthalic acid was 100%, it had a Hazen number of 16, and its 4-carboxybenzaldehyde content was 0.10%.

70 When the finely divided terephthalic acid contained in the mother liquor was isolated and its quality was examined, it was found to have a Hazen number of 160 and a 4-carboxybenzaldehyde content of 0.30%.

Control II

75 Example III was repeated except that a condenser was provided at the top of the oxidation reactor so that condensed aqueous acetic acid solution was recycled to the reaction zone and the terephthalic acid was not caused to crystallise by flashing.

80 The yield of terephthalic acid was 93 mol %, based on para-xylene, its purity was 97%, it had a Hazen number of 250, and its 4-carboxybenzaldehyde content was 1.3%.

WHAT WE CLAIM IS:—

100 1. A process for producing terephthalic acid which comprises oxidising para-xylene in the liquid phase with either molecular oxygen or a gas containing molecular oxygen in the presence of acetic acid and a cobalt-containing catalyst, recovering terephthalic acid by crystallisation from the liquid oxidation reaction product, recycling to the oxidation reaction without distillation the mother liquor, which contains catalyst, remaining after removal of crystalline terephthalic acid, passing the gaseous oxidation reaction product which contains non-condensable gas, water vapour and acetic acid vapour through a fractionating zone in which the acetic acid vapour is condensed while the water vapour is not condensed, recycling the condensed acetic acid to the oxidation reaction and removing the water vapour, together with the non-condensable gas, from the reaction system.

105 110 115 120 125 2. A process according to claim 1 wherein the liquid oxidation reaction product is flashed to cause the terephthalic acid to crystallise, coarse particles of terephthalic acid are isolated and recovered, the mother liquor containing finely divided terephthalic acid crystals is recycled to the oxidation reaction, and the coarse particles of terephthalic

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acid are washed with acetic acid recovered from the flashed vapour.

5 3. A process according to claim 1 or 2 wherein there is used a catalyst containing cobalt, manganese and bromine.

4. A process for producing terephthalic acid substantially as described with reference to the accompanying drawing.

5. A process for producing terephthalic

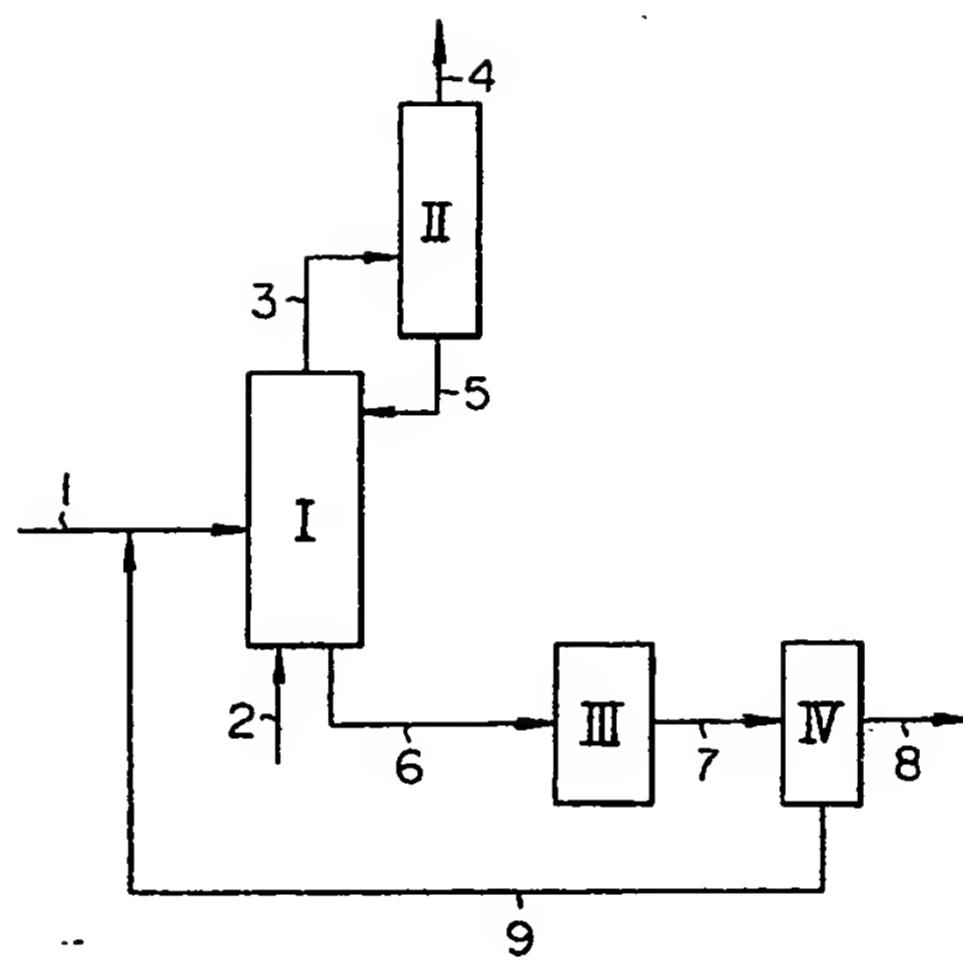
acid according to claim 1 substantially as described in any one of the Examples.

6. Terephthalic acid when prepared by a process as claimed in any one of the preceding claims.

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1373230 COMPLETE SPECIFICATION
1 SHEET *This drawing is a reproduction of
the Original on a reduced scale*



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acid are washed with acetic acid recovered from the flashed vapour.

5 3. A process according to claim 1 or 2 wherein there is used a catalyst containing cobalt, manganese and bromine.

4. A process for producing terephthalic acid substantially as described with reference to the accompanying drawing.

5. A process for producing terephthalic

acid according to claim 1 substantially as 10 described in any one of the Examples.

6. Terephthalic acid when prepared by a process as claimed in any one of the preceding claims.

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